

MEASURES TAKEN AGAINST WATER POLLUTION IN THE KRAFT PULP AND PAPER INDUSTRY

B. HAMMAR and S. RYDHOLM

Billeruds AB, 661 00 Säffle, Sweden

ABSTRACT

Without reclamation of waste liquor and chemicals recovery, the kraft pulp and paper industry would constitute an enormous pollution problem. Already for economical reasons, substantial recovery is secured, however, and considerable further improvements are foreseen. Recovery is outlined in terms of cycles for sodium, calcium, sulphur, and—in a wider sense—carbon. In addition, the mechanical losses of bark fragments and pulp fibres must be observed, calling for a recycling of water and a limitation of the fresh water and effluent volumes. The trend towards higher pulp yields, particularly semichemical pulping, helps to limit the pollution, since less wood substance is dissolved. This refers to kraft pulping as well as to neutral sulphite pulping, which is often combined with the kraft recovery system. Recent machinery developments, such as digesters with countercurrent washing, continuous diffusers and closed screens allowing the screen room filter to be used as a final washer, have all aided in increasing the black liquor reclamation. Developments under way on high-capacity presses are likely to make it almost complete. This has shifted the attention to other pollution sources in bleaching and chemicals recovery.

The elimination of bleach effluents remains to be developed. Oxygen bleaching may become a method for the removal of half the pollution. The considerable extra investment may be compensated by lower operating costs. The continuous diffuser may facilitate the elimination of bleach effluent. Chemicals recovery involves evaporation and combustion of the black liquor and causticizing of the dissolved soda smelt. In the evaporation, volatiles tend to leave the system in vent gases and condensates. Systems have been developed to destroy the vent gases and eliminate the condensate pollution to more than 90 per cent, not counting the occasional entrainment of black liquor droplets, which calls for further improvements in machine design. In the combustion, air pollution is controlled by electroprecipitators and wet scrubbers, but a proper use of the scrubber liquor must be observed. The combination of kraft and neutral sulphite pulping provides such a use, since the scrubber liquor forms the base for neutral sulphite cooking liquor preparation, whereas the kraft recovery system can use the corresponding waste liquor as a sodium make-up.

The kraft papermaking operations lead to fibre losses, which are minimized by recirculation of water. Developments in systems and machine design are needed to improve the situation. Both here and in the recovery system, the temporary losses require increased attention for both pollutional and economical reasons. Improved machine reliability, better process control and production planning are essential factors. In addition to the efforts within the

production processes, pollution abatement must involve effluent treatment. Condensate treatment and particularly fibre reclamation ponds are essential and practical, whereas biological effluent treatment at present is unsatisfactory from both economical and pollution aspects. The recent improvements are evaluated in examples. The current restructuring of the industry offers an ideal opportunity to make use of them, and further efforts are being jointly undertaken by the industry, the financing of which should be in the interest of both industry and society.

INTRODUCTION

The pulp industry will produce about 110 M t this year and is growing at about 5 per cent per annum. The kraft pulp industry will constitute about 60 M t and is the most rapidly expanding pulping process. In production about 60 M t of organic matter are dissolved by about 25 M t of chemicals so that to lose the waste liquor from the process would ruin both the kraft pulp industry and the environment.

Fortunately, it was realized from the beginning of the kraft pulp industry a century ago that this waste liquor, called black liquor, had to be recovered and its chemicals regenerated in order to make the process economical. A technique was borrowed from the sugar industry in that diffusers were introduced, these being large vats where the pulp was washed after the cook with a minimum of water. The reclaimed black liquor was then evaporated in a multistage process to dryness in various types of equipment before undergoing combustion in rotary furnaces. A great improvement in the combustion technique was achieved in the 1930s with the introduction of the Tomlinson recovery furnace into which the black liquor could be sprayed at a dryness of around 60 per cent, thus eliminating the messy operation of drying and dry feeding, and at the same time making it possible to generate large amounts of steam from the recovery furnace. In this way the unbleached kraft pulp mill became selfsustaining with fuel, whereas kraft mills including a bleachery or paper mill still needed additional boilers fired by coal, oil or gas.

In the kraft pulping process, which is essentially a treatment of wood chips with alkali at 170°C for 1–2 hours, the chemicals are used up in the formation of sodium salts of phenolic compounds from the wood lignin and of saccharinic, lactic, and acetic acids from the wood carbohydrates. After combustion of the organics, the alkali appears as a sodium carbonate smelt and is then converted to sodium hydroxide by normal causticizing with lime. In this process, the calcium carbonate or lime sludge formed was for a long time dumped as a valueless by-product, until the technique of lime sludge re-burning was introduced. This is carried out predominantly in large rotary furnaces of the cement furnace type, fired by oil or gas. The re-burned lime is then used again for causticizing. In the recovery process, there is thus one sodium cycle and one calcium cycle.

The unavoidable losses of the sodium cycle were originally covered by the addition of sodium carbonate, hence the name of soda pulping. A century ago it was discovered, however, that sodium sulphate, which was cheaper, could be used as a sodium make-up. This was the origin of the sulphate process, which has since become named the kraft process. In the

recovery, the sulphate was found to be reduced to sulphide, amounting to 25–30 per cent of the carbonate smelt. The sulphide remains unchanged by the causticizing and therefore the cooking liquor, called the white liquor, is a mixture of sodium hydroxide and sulphide.

This mixture was found to be ideal for wood pulping as it accelerated the pulping and resulted in a stronger pulp, useful for the production of both printing and packaging papers. At the same time, it introduced corrosion and air pollution to the alkaline pulping industry, owing to the sulphur compounds of the cooking and recovery operations. Much effort has been spent on the elimination of these problems and also on the elimination of the sulphur again. So far, sulphur is a necessary ingredient of kraft pulping, and there is more hope of eliminating the problems than eliminating the sulphur itself. The measures taken could be characterized as the third recovery cycle, the sulphur cycle.

The organic substance dissolved is thus not recovered but destroyed, and leaves the process as carbon dioxide, both in the lime kiln stack gas and in the stack gas of the soda recovery furnace. In a wider sense, this also represents a cycle, the carbon cycle, since the carbon dioxide is hopefully converted into new forests to produce wood for future pulp production.

The organic substance left after pulping, the pulp fibres, are further treated by screening, cleaning, bleaching and papermaking. During all these operations, which use enormous quantities of water, there is the possibility of mechanical fibre losses. They represent both an economical loss and a pollution problem, and therefore efforts are being taken to recycle the water instead of discharging it as sewage, as was previously the case. In this way fibre losses are contained in the production system. Another mechanical loss of solid organic substances occurs at an early stage in the pulp mill during the wood preparation. The logs are barked in huge barking drums, and until recently they have been sprayed with water to facilitate the bark removal; an excess of this water has been carrying bark fragments out of the system. With dry barking drums, this pollution problem is eliminated, and all the bark is sent for combustion in bark boilers, producing steam for the mill and carbon dioxide to join the carbon cycle.

The bark ashes, as well as dust from the sodium and calcium cycles is a potential source of air pollution, and thus requires special measures.

This survey has illustrated that although the kraft pulping industry represents a huge industrial activity and has a pollution potential of 85 Mt/year, it can exist in principle without environmental danger, if its technology is sufficiently advanced and is properly implemented by engineers and operators. It will be our task now to examine whether these conditions are really fulfilled today, and if not, whether research is in progress to secure this in the future.

PULPING OPERATIONS AND THEIR POLLUTION ASPECTS

Kraft cooking

After the initial modification of alkaline pulping from soda to kraft, the cooking process has remained principally unchanged. Research has mainly brought about an understanding of the reactions between the wood components and sodium hydroxide and sulphide. Recently this has led to some

suggestions for modification of the cooking process to improve the pulp yield, such as the polysulphide, the hydrogen sulphide and the alkaphide processes. They all involve the use of more sulphur and will tend to increase air pollution unless the recovery process is correspondingly modified. This problem has so far retarded development.

A method of yield improvement for all chemical pulping processes is to limit the chemical dissolution of wood substance and to introduce mechanical fiberizing after the cooking—semichemical pulping. This is also carried out in the kraft process, and the pulp yield is normally increased from 47 to 53 per cent, or more. This type of pulp is used for linerboard and now probably amounts to about one third of the present kraft pulp production. Its use is likely to increase, and with some current development efforts the yield level should be improved towards the 60 per cent level. Semichemical kraft pulping decreases the amount of chemicals used and the amount of substance dissolved. Thus, it should help to minimize water pollution.

The most spectacular improvement in kraft cooking machinery is the development of the continuous digester, carried out during the 1950s and 1960s. This allows units of more than 1000 t/d to be built, facilitates instrumentation and automation and gives an operation which can be more easily observed and controlled from all aspects, including pollution. It has been found that the formation of obnoxious gases, which constitutes the main air pollution problem of the kraft mill, is only a fraction of that caused by batch cooking and is more easily collected for destruction in a manner to be described subsequently. Continuous digesters now dominate over the batch digesters in industry, and still more so in the new capacities.

Washing and screening

The initial diffusers used for black liquor recovery were batch operated and required skill and observance from the operators to prevent excessive losses of black liquor to sewer or excessive dilution of the black liquor going to evaporation. After improvement of the diffuser design the losses at reasonable dilution were about 30 kg/t pulp, expressed as sodium sulphate. This unit illustrates that washing of the pulp was initially regarded only from the economical standpoint—the black liquor losses had to be made up for by an equivalent amount of salt cake. The losses from the washing operation are in the form of sodium salts of lignin and carbohydrate degradation products. Some of the sodium is combined with acidic groups still attached to the pulp and is called unwashable or difficultly washable sodium. This amount normally corresponds to 2–5 kg/t, as sodium sulphate.

The introduction of filter washers for the kraft pulp did not improve the washing materially, in spite of 3–5 being used in series, perhaps on average 20 kg/t at reasonable dilution, but they gave a continuous operation, which was more adaptable to control and automation. Also various combinations of filters and presses were tried in the past, usually offering little advantage over pure filter washing with the same number of stages. A great complication with filter washing was experienced, namely the introduction of air into the pulp between the stages, which gave rise to serious foaming problems in the black liquor filtrate tanks. Foam leaving the system has been a constant and

uncontrollable source of pollution. The surface-active agent causing the foam is tall soap, the sodium salts of the fatty and resin acids of the wood.

A considerable improvement was therefore introduced with the digester wash in the continuous digester, whereby the lower part of the digester is used for countercurrent washing instead of pulping. In this manner, the main part of the black liquor is removed, with its tall soap, before the pulp has had any contact with the air. The efficiency of the digester wash is dependent on the retention time, a 4 h retention usually being adequate for a complete digester wash, if 30 kg/t could be accepted. For pollution reasons, this is not the case now, and a more normal system today is a 1–2 h digester wash followed by 2 filters, giving about 15 kg/t salt cake losses.

A recent improvement in kraft pulp washing is the continuous diffuser, which is now rapidly gaining ground in the kraft industry. This machine gives a radial wash through the pulp column after the discharge from the digester at 8–10 per cent consistency. Its effect corresponds to that of 1.5–2 filters and is thus sufficient in combination with a digester wash to give complete washing down to about 15 kg/t salt cake losses.

One further improvement is due to come shortly, with the introduction of closed screening. Until recently, the pulp was screened in an open system, to remove knots and shives. Since screening is usually carried out at 1–2 per cent pulp consistency, enormous quantities of water have been used in this operation. The screened pulp is then normally passed to a medium consistency buffer storage prior to the next operation and must therefore be passed over a filter for dewatering to about 12 per cent. The white water from that operation is then discharged as sewage together with most of the black liquor substance left in the pulp after the washing operation. It is near at hand to use also this last filter for washing, adding the entire wash water at the showers of that filter and passing its white water back for washing and dilution at the previous filter or diffusion washer. This, however, requires screens which can operate in white water without foaming, so-called closed screens. Several such screens have been developed, but additional work is needed to achieve trouble-free operation and satisfactory screening result for all purposes.

With the combination of digester wash, diffuser wash and filter wash after closed screening, salt cake losses at reasonable dilution, 2.5 m³/t, are expected to decrease to about 7 kg/t, not counting the unwashable 2–5 kg/t. This means more than 99 per cent recovery of black liquor, a rather satisfactory result. Further improvements are under way, such as so-called wash presses, where the pulp is subjected to thickening, washing and pressing in one operation. Already in commercial use are thickening presses prior to flash driers. Those presses, from which the pulp leaves at almost 50 per cent consistency, require a fairly high-temperature to be efficient, which calls for a closed system from the medium-density storage. The press water is thus used for dilution of the pulp and excess water can be passed countercurrently to the pulp and used at the first showers of the filter washer prior to the storage tower. For unbleached flash-dried pulp, this would give an entirely closed system with almost 100 per cent black liquor recovery, if only all minor flows, such as filter wire showers, can be kept under proper control. Some development work is still required here.

In essence, the same complete recovery of black liquor would also be possible with unbleached kraft pulp going to an integrated paper mill for unbleached kraft paper and board, assuming that it would be acceptable for those products to contain the residual black liquor substance. This is not always the case, for instance with papers used for electrical insulation purposes which demand low conductivity. There are also other complications, which will be discussed later.

Bleaching

Kraft pulp bleaching has developed considerably after its major breakthrough in the 1930s, when multistage bleaching with chlorine, alkali and hypochlorite was introduced. The introduction of the chlorine dioxide finishing stages in the 1940s and some later simplifications have left us with two standard bleaching schedules now universally applied, namely (C for chlorination, E for alkali extraction, H for hypochlorite and D for chlorine dioxide):

/C/E/H/D/E/D/ for softwood kraft pulp and

/C/E/D/E/D/ for hardwood kraft pulp

In some cases also sodium peroxide has been added with advantage to a caustic extraction stage, and in other cases some reversal of stages is preferred.

Bleaching is now always continuous in upflow or downflow towers, with subsequent filter washing. Apart from the chlorination which should be at room temperature and 3–4 per cent consistency, all stages are preferably hot and at medium consistency, about 10–14 per cent, and intermediate transport is carried out by thick stock pumps. Both heat economy and chemical economy are essential in the bleaching. Whereas the former may be improved by closed operation of the white water systems of the filters, chemicals economy favours efficient washing, which is improved by opening the water systems. The recent continuous diffuser for radial diffusion washing at 8–10 per cent consistency, which is now being introduced to bleaching in upflow bleach towers, may lead to more efficient washing and more sophisticated systems for countercurrent washing and water usage throughout the bleachery. In principle, the wash water should enter at the last, or the last two stages, and the bleach effluent leave at the chlorination and first alkali extraction stages, where the main dissolution of matter takes place. The dissolution of organic matter during bleaching is only about 7 per cent of the pulp with softwoods and about 3 per cent with hardwoods, compared with about 110 per cent in the cooking. It is thus obvious that when the black liquor is recovered to 99 per cent in the washing operations whereas the bleach waste is not recovered, it makes the bleach effluent the larger source of pollution in bleached kraft mills.

Admittedly, the organic substance leaving the bleachery is partly oxidized, but it will still continue to consume oxygen in the recipient. It is also yellow to brown in colour and may therefore occasionally be a conceivable source of discoloration of the recipient in further use. A disadvantage only in acid regions is the sodium chloride formed in the bleaching operation from the chemicals used.

There are at present two approaches to this effluent problem. One considers the precipitation of the effluent. This requires an effluent which not too

dilute and a cheap precipitant. The water economy made possible by the diffusion washer may open a possibility here, and lime has been shown to precipitate part of the organic substances. The lime consumption appears to be high, however, and the problem of sludge separation and destruction is likely to be formidable. The precipitation method is therefore held to be less promising and also represents an entirely unproductive solution from an economical standpoint.

A more promising approach is the oxygen bleaching method, which is on the verge of a break-through now. This method was initially developed from the laboratory stage for those mills in arid countries, the effluents of which are used in irrigation and where sodium chloride is objectionable. It aims at substituting chlorine for oxygen in the initial degradation of lignin, thereby eliminating the main source of sodium chloride from the effluent. So far, however, this does not seem to be possible, if the present quality demands for brightness and paper strength are to be maintained. For the present, therefore, a combination of oxygen bleaching and chlorination appears to be the realistic approach, with the oxygen stage prior to the conventional multistage bleaching. This could eliminate about half of the organic substance from the bleachery effluent, provided a suitable system is worked out for passing the effluent of the oxygen stage countercurrently to the pulp into the black liquor washing system. That in turn calls for the elimination of acidic pretreatments which have been suggested for the elimination of the peroxide decomposition catalysts, such as heavy metals, known to be detrimental to the oxygen bleaching result. Systems are being devised for this at present.

Should this succeed, about half of the bleachery effluent will be eliminated, at the cost of a rather heavy investment in machinery for a pressure operation and washing prior to a normal bleachery. However, there is considerable hope that this investment could be justified by savings in the bleaching chemical costs and would then represent a development of the desirable type in pollution abatement, one combining economy with environmental care.

CONSUMPTION AND REGENERATION OF PULPING CHEMICALS

Evaporation of black liquor

The reclaimed black liquor from the kraft cooking contains about 16 per cent dry matter and has to be concentrated before combustion. This is done by indirect steam multistage evaporators, 5-6 stages. According to Scandinavian practice, the evaporation is carried to 60-65 per cent dry substance, and the thick liquor sprayed directly into the recovery furnace, whereas American practice so far favoured a system where the multistage evaporation gives only 45-55 per cent concentration. In that case the thick liquor is introduced into a direct contact evaporator for final thickening to almost 70 per cent by hot stack gases. This gives a lower investment but leads to an air pollution problem, since the stack gases carry obnoxious compounds from the black liquor to the atmosphere. The future American industry is likely to adopt the Scandinavian system.

The evaporation creates two pollution problems. Some non-condensable gases and volatiles are stripped off the black liquor, mainly hydrogen sulphide, methyl mercaptan and dimethyl sulphide. According to recent measurements, they correspond to a sulphur content of about 0.3–1.0 kg/t pulp. Alkaline absorption in a Venemark scrubber, for example, is being used, but is effective mainly on hydrogen sulphide. This is still an advantage with the tail gases of the evaporation, whereas the organic sulphides should be recovered in the condensers prior to the vacuum pump as condensates for further treatment.

Another way of decreasing the loss of sulphur compounds in the evaporation is black liquor oxidation. This operation involves the aeration of black liquor in order to convert inorganic sulphides to thiosulphate and mercaptan to dimethyldisulphide, thus decreasing their volatility in the evaporation. This is particularly valuable in combination with the previously mentioned final direct-contact evaporation but has the drawback of leading to a loss in heat value of the black liquor of 100 Mcal/t pulp. Since black liquor oxidation requires both investment and operating costs without materially improving the Scandinavian system, it is decreasing in importance, particularly since its corrosion-inhibiting effect is negligible with modern evaporation equipment using stainless steel.

Whereas the previous phenomenon leads to air pollution from the evaporation unless proper precautions are taken, the condensates present a water pollution problem. The condensates have an unpleasant odour from hydrogen sulphide, methyl mercaptan and dimethyl sulphide, but contain also other organic compounds, mainly methanol and terpenes. All the components represent a considerable source of biological oxygen demand in the recipient.

The condensates from all effects are contaminated, but to a varying degree. The first part to become treated was the tail end condensates from the fifth effect. The previous system with direct condenser and water jet vacuum pump used large volumes of water and made water pollution unavoidable. After the introduction of surface condensers and water ring pumps or steam jet pumps it has become possible to collect the tail end condensate for destruction together with the digester flash condensates.

The rest of the evaporation condensates are normally combined and used as much as possible in the causticizing and sometimes pulp washing operations. However, only about $\frac{1}{3}$ of the volume can be used in the causticizing, and there will be other water sources for pulp washing, as previously mentioned. It was therefore of interest to learn recently at the kraft mill in Gruvön, that the condensates of the steam from effects 1–2, which are the last ones in the flow of the black liquor, are practically pure and should thus not be combined with the rest of the condensates but could be discharged to the sewers. The major part of the remaining, contaminated condensates could then be placed in the causticizing, and a particularly contaminated fraction could join the tail end condensates and digester condensates for destruction.

The condensate destruction is now carried out by the Skoghall method of column stripping followed by combustion of the evil-smelling compounds in a boiler or lime kiln. The methanol destruction at Gruvön is estimated to become 90 per cent through these precautions and for the more volatile sulphur compounds the elimination is still more complete. The biological oxygen demand thereby prevented is in the order of 7–10 kg/t pulp.

An important source of water pollution over the evaporator condensates is the foaming and entrainment of the black liquor in the evaporators. In addition to proper mechanical separation devices, it is also now required to keep the conductivity of the condensates under control and to sound an alarm for improving the evaporation whenever contamination with black liquor occurs.

Black liquor combustion

The recovery furnace of modern construction is a combination of a chemical reactor and a boiler and draws an investment cost of 4–5 times the cost of an oil-fired boiler of the same steam production. With high-yield pulping, particularly neutral sulphite pulping, the amount of organic substance and hence the steam production is so small that a recovery boiler may be considered too expensive. Then destruction furnaces of simpler design may be used, but they are outside the scope of this paper, since the kraft process is not operated in that yield range and since the neutral sulphite process will only be considered in combination with a kraft mill, so-called cross recovery, with the combustion of the combined liquors in an ordinary recovery furnace.

The combustion of the black liquor does not give rise to any direct water pollution, but the stack gases formed may contribute to the contamination of our lakes and therefore have to be controlled. Recent measurements at 10 kraft mills carried out by the joint air pollution committee of the Swedish authorities and pulp industry, show that the only detectable gas pollutants in the recovery stack gases are hydrogen sulphide and sulphur dioxide. The measurements have indicated that by proper control it might be possible to keep the hydrogen sulphide content at or below 1 ppm.

The sulphur oxides of the recovery stack gases prior to any washing amount to the order of 6–12 kg/t pulp, expressed as sulphur. The relative sulphur loss appears to increase linearly with the sulphur : sodium ratio of the black liquor. Therefore, a stack gas washing to reduce the sulphur emissions will be of limited effect. If the sodium make-up remains sodium sulphate, a flue gas scrubber, with the wash liquor excess being passed to the chemicals recovery cycle, will only cause a build-up of sulphur and finally emission of the same amount of sulphur as without a scrubber. To pass the wash liquor to the sewer would only expediate the process of converting the air pollution to water pollution.

The only possibility is to exchange the make-up sodium sulphate for a sulphur-free sodium compound, at least partially. One large Swedish kraft mill with a 95 per cent sulphur dioxide recovery from the stack gases, including those of odor compound combustion, has had to substitute 60 per cent of the make-up sulphate with soda to maintain normal sulphidity in the cooking liquor. The sulphur emission was then reduced to below 100 t/year or below 1 kg/t pulp.

Causticizing

The smelt flowing from the lower part of the recovery furnace contains mainly sodium carbonate and sulphide. After dissolution, this mixture is called green liquor and is causticized by lime to give white liquor for cooking

and a lime sludge. After the introduction of the lime kiln, the only waste product from the causticizing is some solids, lime grit and green liquor dregs, insoluble inorganic impurities in limited amounts, which are separated and dumped on land.

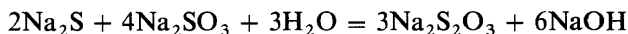
Cross recovery

It is a natural and accepted demand today that sulphite waste liquor must be recovered and burnt. With lime-based mills, this results in a sulphur emission of over 60 kg/t pulp, which on the other hand produces unacceptable air pollution. Transformation to soluble bases with chemicals recovery will thus be necessary during a transition period. With sodium base, combination with kraft mill recovery appears to be particularly attractive, since it allows joint use of the expensive evaporation and combustion facilities.

In its simplest form, cross recovery means the addition of the sodium-based sulphite waste liquor to the kraft recovery system where its sodium content is used as the make-up for losses in the sodium cycle of the kraft recovery. Then the sulphite cooking liquor can be made from fresh chemicals. Such a system obviously seriously limits sulphite pulp production at a set kraft pulp production with certain sodium losses. To increase the ratio of sulphite to kraft pulp, a special process is required to convert the sodium sulphide of the green liquor in part to sulphite or bisulphite for the sulphite mill. Those processes will be described in a separate presentation. Only the special case of the neutral sulphite process will be dealt with here where particularly simple methods can be used.

Normally, the neutral sulphite cooking liquor contains $\frac{2}{3}$ sodium sulphite and $\frac{1}{3}$ sodium carbonate. It is possible to substitute nearly all the soda buffer with green liquor. Also, if the sulphite is produced internally by the absorption of sulphur dioxide by alkali in the flue gas scrubber, a considerable decrease in the sulphur emission of the kraft mill can be achieved without abnormal sulphidity within a very wide range of ratios neutral sulphite: kraft pulp.

A further widening of the range of this capacity ratio is achieved by using a Billerud variety of the IP recovery method. In the latter, sodium sulphite is prepared from green liquor by introducing sulphur dioxide gas in a stripping column and withdrawing the hydrogen sulphide formed for combustion to more sulphur dioxide. This crude method accepts considerable thiosulphate formation from the side reaction



The rate of this reaction is strongly pH-dependent, and when the green liquor use is limited to the buffer, one third of the cooking liquor, there is practically no reaction between sulphide and sulphite. If, however, green liquor is treated with considerable amounts of sulphur dioxide, the bisulphite ion formed will rapidly react with the sulphide to thiosulphate. The rate increases with the sulphite concentration. Even if the neutral sulphite cooking process can tolerate some thiosulphate without serious disadvantage, the thiosulphate represents an inert sodium compound, which increases the load on the recovery cycle and leads to higher losses of sodium and sulphur.

The Billerud method therefore tries to strip off the hydrogen sulphide at the lowest possible sulphite concentration. The initial acidulation is thus

made by a precarbonation of the green liquor with lime kiln gases. The small amount of hydrogen sulphide stripped in that operation is reabsorbed by white liquor at the top of the column and this white liquor can be used in the kraft cooking without any conversion. The precarbonated liquor is heated to boiling and then presulphited by dilute SO_2 gas in another column under contemporary introduction of stripping steam. The stripped hydrogen sulphide is then burnt together with make-up sulphur in a furnace. Part of the hot, moist gas is returned for presulphitation, and the remainder cooled and used for final sulphitation in the main sulphur dioxide absorber.

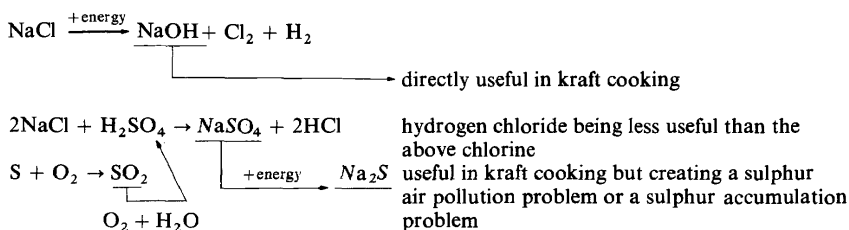
In this manner, a neutral sulphite cooking liquor of good quality can be prepared, using only minor amounts of fresh chemicals and allowing cross recovery systems where the neutral sulphite pulp production is at least as large as the kraft pulp production. The two pulping processes might be said to complement each other in an excellent manner on the chemicals recovery side, since the neutral sulphite process allows the use of the absorption liquor from the scrubber of the recovery stack gases, and the kraft regeneration system can make use of the sodium of the neutral sulphite waste liquor as a make-up for sodium losses.

Make-up chemicals in the kraft recovery cycle

When the soda process changed into the kraft process, the make-up chemical was changed from sodium carbonate to sodium sulphate. With the increased emphasis on water pollution aspects and the decreased sodium losses of an efficient black liquor recovery, the sulphidity of the smelt and cooking liquor tended to decrease towards the lower tolerance limit, 20 per cent, as long as the air pollution was of no concern. Kraft mills even had to add elemental sulphur to keep up their sulphidity. With increased concern about air pollution and the addition of stack gas scrubbers to the system, sulphur has started to increase to the upper tolerance limit of sulphidity, about 40 per cent, as long as sodium sulphate is maintained as the make-up chemical. Consequently, part of the make-up should be sulphur-free, but this involves extra cost as long as salt cake is the cheapest sodium compound (not counting sodium chloride, which is unsuitable). The combination with a neutral sulphite mill creates a useful and economic introduction of partly sulphur-free sodium compounds. That can with extra advantage be added to the flue gas scrubber for sulphur dioxide absorption, since it has been found that the normal addition of white liquor to the scrubber adds to the hydrogen sulphide of the flue gases in an unacceptable manner.

For kraft mills not possessing cross recovery with a neutral sulphite mill, the use of some sulphur-free sodium salt to decrease the air pollution will mean considerable extra costs, unless the world-wide imbalance in the chlorine-alkali situation lowers the alkali price to a level corresponding to that of salt cake. Considering that both chemicals originate from sodium chloride along two separate paths (see p. 274), the one leading to salt cake being more complicated, such a development does not seem unreasonable.

On the other hand, if oxygen bleaching develops in the anticipated way, this will decrease the chlorine consumption and increase the alkali demand, thus tending to restore the chlorine-alkali balance and keep up the alkali price.



Another source of alkali in bleached kraft mills is the residual liquor of the chlorine dioxide generation, which consists of essentially sodium bisulphite and sulphuric acid. If salt cake has a potential 100 per cent sulphidity, that liquor holds 2–300 per cent and thus adds to the sulphur problems, when that liquor is added to the recovery cycle. For a kraft mill bleaching its entire production, the liquor corresponds to about 15 kg/t of salt cake and 8 kg/t of sulphur, which is a substantial portion of the make-up and may require special attention otherwise air and water pollution aspects will conflict again.

KRAFT PAPERMAKING OPERATIONS AND THEIR WATER POLLUTION ASPECTS

In the paper machine, the beaten stock is dewatered from 0.2–0.8 per cent to 33–50 per cent consistency after the press section. In addition to this, a further quantity of water used in the showers at the wire and press felts has to be removed. With no recirculation the water consumption would therefore be of the order of 1000 m³/t paper and the fibre losses unacceptable. A large volume can be recycled with no particular difficulty, and the water consumption reduced to the order of 100 m³/t.

It has been found that the fibre losses have a direct relation to the water consumption, and it is thus desirable to reduce the water consumption still more. One possibility would be to use excess water from the paper machine system for dilution in the screen room and for the transportation of thickened pulp to the paper mill. However, this would mean that the pulp arrives at the beating department with water containing paper chemicals such as alum and sulphuric acid. That is undesirable since the beating should be carried out with the pulp in the slightly alkaline state of swelling that still prevails after washing.

Therefore, the use of white water from the paper machine should be increased in the operations around the machine, for dilution after beating and in the showers. The latter requests both a shower nozzle design insensitive to fibres and at least a partial fibre removal of the white water. A well closed white-water system, on the other hand, also leads to a temperature increase at the wet end and press section that may result in a 1–10 per cent production improvement without additional steam consumption. This may often pay for the investment needed in closing the white-water system.

Methods dealing with the internal white-water purification and fibre recovery have been surveyed in detail by the fibre committee of the Association of Swedish Pulp and Paper Engineers. Information has been gathered

and arranged for a large number of paper-machine systems and their save-all machinery. It is difficult to state any minimum for the water consumption at the paper machine since slime generation, for example, and other production difficulties tend to limit the possibilities of closing the system. 'Specific water consumption' also appears to be a dubious concept, since it is highly dependent on the machine size. For a modern paper machine of reasonable size, it should be possible to reach 20–30 m³/t paper, whereby the fibre losses should be less than 0.5 per cent.

Great attention is paid today to the use of flocculants and retention aids, both at the paper-machine wet end and in subsequent fibre reclamation systems. Particularly neutral sulphite pulp contains matter of colloidal character, which can be flocculated. Increasingly specific high-polymer flocculants are being produced, at initially excessive prices, which are now decreasing.

For the save-alls, new constructions are continually tried, according to all three methods used in the past: filtration, flotation and sedimentation. The fibre committee just mentioned has made a literature survey and an equipment compendium to clarify the present technological position. Each case requires specific application of the existing knowledge, and no general solution has been advocated.

PRODUCTION CONTROL AND SO-CALLED TEMPORARY LOSSES

A considerable part of the total pollution from a kraft pulp and paper mill is caused by so-called accidental or temporary losses. These are often brief but with the high production rate of a modern mill they may yet involve quantitatively large losses, which also increase in proportion to the normal losses with greater efficiency in steady state recovery.

Production disturbances, causing buffer storage tanks to overflow, are a major source of temporary losses. Even modern pulp and paper mills have been shown to lose as much as 1–2 per cent of their production in temporary losses through overflowing. It is not only the unexpected disturbances that lead to temporary losses, but planned routines may also have this effect, such as changes in the production level. The losses then occur mainly during the period of change, i.e. until a new steady state has been reached.

Disturbances and the consequent temporary losses can certainly not be eliminated entirely. However, both their frequency and duration and thereby their consequences can be substantially reduced by a close control not only of the processes of the various departments but also of their coordination, production control. The recent development of the process computer technique has supplied new possibilities here. Billerud has together with IBM developed a computer-based system for process and production control of an integrated kraft pulp and paper mill which is now in use. Starting from a sales-directed paper production plan, production schedules for the various processes are calculated, which will give a minimum of production changes and a maximum utilization of available buffer capacities. The computer technique is also utilized for the direct control and supervision of several of the processes involved. The production changes of these processes are

thus rapidly and smoothly performed with the aid of the computer. The system is presently being expanded to integrate more of the recovery system, where now the evaporators and soon the recovery boiler will be controlled by the computer.

The present development in the process industry towards the systems concept and more advanced production and process control is thus likely to have a positive influence on environmental care also, minimizing both the steady-state pollution and particularly the so-called temporary losses.

PURIFICATION OF EFFLUENTS

Type of effluents

In spite of all efforts to limit the losses of inorganic and organic matter from the various processes, a certain effluent is unavoidable from the kraft pulp and paper mill. The most noteworthy categories are:

(a) Volatile sulphur compounds, predominantly methyl mercaptan, dimethyl sulphide and diethyl disulphide. In addition to their unpleasant odour, they are poisonous and tend to give a bad taste to fish even at low concentration.

(b) Biologically oxygen-demanding substances, mainly the methanol of the evaporation condensates and carbohydrate degradation products of the black liquor not reclaimed for combustion.

(c) Lignin from the same black liquor residues and also from the bleaching. The role of the lignin in the recipient is still unknown and subject to current investigations at IVL and other places.

(d) Fibres from the various operations. The fibres are initially a local problem, since sedimentation occurs in the recipient close to the mill. Eventually, biological activity will develop in such fibre banks, causing a local oxygen deficit, gas evolution with fibre cakes rising to the water surface and other undesirable phenomena.

Therefore, depending on the internal measures taken to minimize the losses, on the capacity of the recipient and other local conditions, effluent purification of varying degrees can be motivated. In certain cases there are acceptable methods, in other cases considerable development work is required. It should always be kept in mind that the most efficient and at the same time most economical methods of preventing pollution are measures taken in the production processes, before the substances become mixed and diluted with large amounts of effluent water.

Condensate treatment

The condensates of the cooking and evaporation operations have previously been discharged to the sewers. They contain volatile sulphur compounds, methanol and terpenes. As mentioned previously, part of the evaporation condensates are practically clean and should not be combined with the dirty ones. The latter should join the digester condensates for condensate treatment according to the Skoghall method before being discharged to sewers. This method has proven to be efficient, and at a sacrifice of 0.16 t steam per t condensate a 90 per cent stripping of methanol and above 99 per cent

removal of sulphides is obtained. This corresponds to the theoretical expectations and proves that the presence of terpenes aids rather than prevents the stripping. As a rule a larger removal of BOD substance is achieved than corresponds to the methanol, indicating the presence of emulsified terpenes. The subsequent combustion of the volatile substances in the recovery boiler or lime kiln has been found to be complete.

Fibre ponds

Irrespective of the extent of internal closing of the white-water systems, the authorities now request that all effluent carrying fibres shall be sent to settling ponds. For conventional design with a depth of 2 m, a surface load of 1.5 m/h is usually allowed. It is considered that rectangular ponds give a more ideal flow but that circular ponds are safer in operation. However, the new pendulum scraper design in the fibre ponds recently installed at Gruvön has given very positive results. Vertical sedimentation designs, allowing loads of up to 3 m/h and the elimination of mechanical scrapers, have been installed at several mills with varying success. Still higher loads can be achieved with lamellar sedimentation. There is no full-scale plant in operation yet, but it is hoped that this development will further reduce the size of the sedimentation ponds, which today occupy a seriously large area of valuable mill site.

The most essential future design task may not be that of the ponds or scrapers but the handling of the reclaimed fibres. If this handling does not function at the rated capacity, the fibre ponds will not be emptied and thus not perform. Various types of presses are available but they generally require a dewatering prior to pressing, and are also subject to hard wear. The water from the sludge contains fibres and should be sent back to the ponds, possibly after an addition of flocculants. Billerud has been trying another solution at Gruvön for a few months. The pond sludge is pumped through knotters and vortex cleaners to the paper mill for fluting production. The system operates well, but it remains to be seen whether it produces any disadvantages in production rate or product properties.

Biological purification

Biological purification of kraft mill effluents was investigated by Billerud at Gruvön 10 years ago in a pilot plant of 1 m³/min capacity. It was shown that all effluents from the kraft mill can be treated, provided the bleachery effluent is deaerated in advance to prevent the chlorination of the biological sludge. An elimination of 85–90 per cent of the immediate BOD was achieved in undisturbed operation, but it was found that only 30 per cent of the phosphate added to maintain the biological process was absorbed by the sludge.

Today, such a purification method is considered meaningless. The phosphate transferred to the recipient in this manner gives rise to biological activity, which including algae gives an oxygen consumption of the same order of magnitude as the organic substance removed from the effluent. Biological purification will thus have to be combined with chemical precipitation. In order to study the technical prospects of such a process, IVL and several companies have started to co-operate, and a pilot plant of 5 m³/h will be operated at the Fiskeby pulp and paper mill of Skärblacka, where kraft, neutral sulphite and acid sulphite effluents are available.

Preliminary cost calculations based on laboratory trials and experience abroad indicate that the process will be very expensive. For a combined kraft and neutral sulphite mill of the size of Gruvön, the investment will probably be about 16 M Sw. crs and the operating costs about 7 M Sw.crs/annum, which is almost prohibitive, since there will be no economical savings from the process. Furthermore, the bacterial sludge formed is likely to present a delicate disposal problem, and finally the lignin content of the effluent appears to be only slightly reduced after reasonable treatment periods.

Lignin removal

In a modern kraft pulp mill it should be possible by a combination of efficient washing and condensate treatment to reduce the BOD substance losses to 5–10 kg/t pulp. The total losses of lignin at conventional bleaching are about 50 kg/t pulp. Therefore, an increased knowledge of the behaviour of lignin in the recipient and of improved methods of lignin elimination are now required. Work is in progress at North American institutes and elsewhere. The methods on trial are lime precipitation, flocculation with aluminium or iron salts, active carbon adsorption, electro dialysis, inverted osmosis and biological methods.

Lignin of bleachery effluents is difficult to precipitate, which makes the amounts of lime or flocculants formidable. The colour reduction is rather good but the removal of total lignin substance poor. The membrane processes are interesting and maybe the most elegant ones for the future, when sufficiently durable and inexpensive membranes have been developed. Since the same processes are being developed for the more universal problem of desalting of sea water, it is likely that our industry may benefit from those advances. So far, the most promising approach to lignin reduction from bleachery effluents is the oxygen bleaching previously mentioned.

TOTAL POLLUTION OF A KRAFT MILL

In order to demonstrate the relative importance of various methods of pollution control, a practical example will be given here. Take, for example, a large mill producing 500000 t/annum of kraft pulp and paper, half of which is bleached, and compare it with another mill of the same size, producing unbleached and bleached kraft papers, kraft liner board and neutral sulphite fluting, with the following pulp production ratios:

Bleached kraft	25 per cent
Unbleached kraft	15 per cent
Semichemical kraft	35 per cent
Semichemical neutral sulphite	25 per cent
	100 per cent

The former mill is assumed to have reasonably good black liquor recovery, with salt cake losses in the washing of 25 kg/t pulp, but no condensate treatment, no internal white-paper purification with fibre reclamation but the normal fibre ponds.

POLLUTION CONTROL IN THE PAPER AND PULP INDUSTRY

The latter mill is assumed to apply cross recovery, to use closed systems as much as possible and effluent purification according to the following alternatives:

(1) Conventional bleaching, condensate partition with the most pure condensates discharged to the sewer, the intermediate ones recycled (to the causticizing) and the most impure ones to stripping. Maximum closing of the white-water systems and internal fibre reclamation.

(2) As case 1 but also biological treatment (85 per cent purification) of the sewered condensates and the fluting mill effluent, but not the bleachery effluent.

(3) As case 1 but biological treatment of all BOD-containing effluent.

(4) As case 1 but with an oxygen stage prior to the conventional bleaching to take care of half of the substances dissolved in the bleaching and transferring them to the black liquor for normal combustion.

Table 1. Water pollution in the production of 500 000 t/annum of pulp and paper, employing different product mix and purification methods.

	1960	1970			
	Kraft pulp and paper	Kraft and NSSC pulp and papers			
		Case 1	Case 2	Case 3	Case 4
Production, 1000 t/annum					
Kraft: bleached	250	125	125	125	125
unbleached	250	75	75	75	75
semichemical	—	175	175	175	175
NSSC	—	125	125	125	125
Total	500	500	500	500	500
Water consumption, m ³ /t	250	54	54	54	54
Fibre losses, t/d	27	6	6	6	6
BOD ₇ , t/d	66	17	11	5	15
Lignin, t/d	58	16	16	13	10
BOD ₇ + lignin, t/d	124	33	27	18	25
Total pollution, t/d	151	39	33	24	31
Biological treatment	—	—	part	complete	—
Oxygen bleaching	—	—	—	—	part

The results are shown in *Table 1*. It is obvious that by efficient washing, closing of the systems, condensate partition and treatment, and not least the introduction of high yield pulps, the pollution can be reduced to 20–25 per cent of that of the conventional kraft mill of the 1960s. Biological treatment results in a further slight reduction of the BOD, particularly if all effluent is treated (3 M Sw.crs./annum plus capital costs), but with a rather insignificant lignin reduction. Partial oxygen bleaching would reduce the lignin pollution by 40 per cent and since the BOD will be only slightly higher than with the partial biological treatment, the total pollution will be lower in that case, and further development work may improve the figures still more. Since the investment cost of an oxygen bleaching stage will be of the order of 10 M Sw.crs. as compared to 16 M Sw.crs. for a biological treatment and it

results in no sludge disposal problem or additional operating costs, this line of development appears to be the more sensible one.

It seems, therefore, wise to concentrate on the development of oxygen bleaching and to introduce the recently developed systems of condensate partition and treatment as well as a systematic closing of the white-water flows. The biological methods still appear to require more attention and basic research on the laboratory and pilot stage to overcome fundamental technical and economical drawbacks.

CONCLUSIONS

The pulp and paper industry is a highly competitive one and, although it is still growing fairly rapidly, there is a current and accelerating restructuring, whereby small and medium-sized mills have to be closed down in the competition with larger and more rational modern units. In this process, there is a good chance that the modern demands for less pollution will be observed, if only the means of improving the situation are realized early enough in the planning of the new industry.

Recent surveys of the water and air pollution situation in Sweden, including the new techniques for minimizing the emissions, have been made by collaboration between authorities and industry. A joint industry committee has recently been formed, which aims to further develop interesting techniques in some typical pulp and paper mills. This will be done in jointly financed projects, the results of which will be accessible to the industry. The contributions of the machine manufacturers will also be secured.

Those projects will supplement the more fundamental laboratory investigations of the Swedish Forest Products Research Institute and IVL, both in Stockholm, which are now jointly financed by state and industry. So far, it has not been possible to secure much government money for the large-scale practical projects. It is hoped that now that industry has engaged on a practical and wide programme to lay the foundations for pollution control of future mills, it will be realized and demonstrated in active financing that it is in the interest of both society and industry to design the future export industry for both economic competitiveness and good environmental care.